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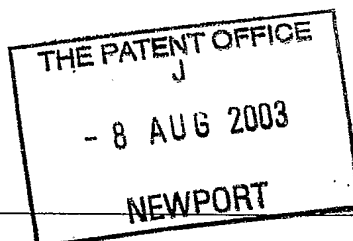
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08AUG03 0826888-1 004171
P01/7700 0.00-0318644.2

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



The Patent Office

Cardiff Road
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NP10 8QQ

1. Your reference

LEX P03/1

2. Patent application number

(The Patent Office will fill in this part)

08 AUG 2003

0318644.2

3. Full name, address and postcode of the or of each applicant (underline all surnames)

GILMOUR ALEXANDER

357 2757002 35 MANOR ROAD
HENLEY-ON-THAMES
OXON RG9 1LU

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

LEXCEL TECHNOLOGY LTD, ENGLAND

4. Title of the invention

ELECTROCHEMICAL CELL HAVING "IN SITU" GENERATED COMPONENT

5. Name of your agent (if you have one)

NONE

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Graham Jones & Co
77 Beaconsfield Road
Blackheath
London SE3 7LG

35 MANOR ROAD
HENLEY-ON-THAMES
OXON RG9 1LU

Patents ADP number (if you know it)

2097001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

N/A

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

N/A

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
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- See note (d))

No

Patents Form 1/77

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Description	3
Claim(s)	1
Abstract	1
Drawing(s)	212

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Priority documents	NONE
Translations of priority documents	NONE
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	NONE
Request for preliminary examination and search (Patents Form 9/77)	1
Request for substantive examination (Patents Form 10/77)	NONE
Any other documents (please specify)	NONE

11. I/we request the grant of a patent on the basis of this application.

Signature

Alexander Gilmore

Date 7/08/2003

12. Name and daytime telephone number of person to contact in the United Kingdom

A. GILMOUR 01491 874414

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Electrochemical cell having "in situ generated" component

ABSTRACT

The present invention relates to an electrochemical cell having a solid polymer separator/electrolyte whose ion conductivity is markedly increased by in situ generation of a fluid acidic anhydride.

The cell according to this invention comprises a solid polymer electrolyte, an anode of an alkali or alkaline earth metal such as lithium and a cathode containing the lithium or other alkali or alkaline earth metal salt of the acid anhydride to be electrochemically generated in addition to the main active material. The salt which is central to this invention has the formula MA_xO_y where M is an alkali or alkaline earth metal in particular lithium and A is a non metallic element such as sulphur, nitrogen, carbon or phosphorous $0.5 \leq x \leq 2.0$ and $2 \leq y \leq 4$. The cell according to this invention has much improved rate capability and low temperature performance but no liquid constituents are required for assembly of the cell.

Background to the invention

The electrochemical cell according to this invention shows a marked increase in rate capability, particularly at low temperatures and has the significant advantage that no liquid constituents are required in manufacture.

The present invention is concerned with enhancement of the ionic conductivity of a solid electrolyte particularly for rechargeable batteries and supercapacitors, obviating the need for organic solvents which are expensive and being flammable, constitute a safety hazard in large batteries.

Solid electrolytes, particularly those based on organic polymer compositions which contain basic sites (ether, secondary or tertiary amine etc.), are now gaining favour in lithium rechargeable battery technology as a viable alternative and replacement for liquid electrolytes having a high percentage of organic solvents.. The ionic conductivity of these electrolytes is however inferior to that of the liquid types and is not acceptable for high rate, low temperature applications. Many so called "solid electrolyte" cells have indeed a significant amount of polar organic solvents added in order to raise the conductivity to acceptable levels. Such electrolytes with added solvents are typically in the form of a viscous gel which is tacky and sticky and makes electrode assembly into cells a difficult operation. This electrolyte must also be added to both the anode and cathode compositions in order to achieve acceptable ionic conductivity.

The use of an acid anhydride as a major electrolyte constituent in non-aqueous batteries was first demonstrated by American Cyanamid in the 1960's with a succession of patents involving the use of sulphur dioxide as both electrolyte vehicle and cathode with lithium or other alkali metal as anode. A considerable amount of research and development work was carried out over the ensuing 25 years, mainly in the USA towards the utilisation of this novel chemistry for both primary and secondary batteries. Several companies were successful in the production of lithium sulphur dioxide primary cells but their use was mainly restricted to military applications. Although a viable rechargeable battery based on the same chemistry was never realized, a sulphur dioxide based electrolyte used in conjunction with a lithium cobalt oxide cathode has been demonstrated for high rate applications, the ionic conductivity of the sulphur dioxide electrolyte used being

an order of magnitude greater than in existing organic solvent based electrolytes. The volatility of the sulphur dioxide electrolyte has precluded its use in most consumer applications, this accounting for the virtual cessation of further R&D work on sulphur dioxide chemistry for battery applications.

Detailed description of the invention

The present invention brings together the ease of manufacturing and leak resistance advantages of solid electrolytes with the performance enhancement due to the presence of sulphur dioxide or related acidic anhydrides in the electrolyte. Sulphur dioxide is generated at the cathode on charging the cell and at the same time, lithium metal is electroformed at the anode. The solid electrolyte chosen for the implementation of this invention has a structure with basic functional sites which associate with sulphur dioxide to give a non-volatile network which facilitates lithium ion conduction.

A section of an electrochemical cell embodying this invention is shown in Fig 1. Referring to Fig. 1, the positive current collector **12**, consists of aluminium foil typically 15 microns thick to which is bonded the active cathode **13**. The most widely used material for the cathode is a lithiated intercalation compound such as LiCoO_2 , carbon black or graphite and a polymeric binder such as poly(vinylidene difluoride) PVDF. The main feature of this invention is the addition of the lithium salt of a sulphur oxy-acid to the cathode formulation. The additive may be chosen from one of a number of lithium sulphur oxy-acid salts, particularly lithium dithionite $\text{Li}_2\text{S}_2\text{O}_4$, or lithium sulphite Li_2SO_3 , added in a proportion of up to 10% by weight of cathode.

The negative current collector **18**, consists of copper foil typically 12 microns thick to which the anode material **17**, consisting of meso carbon or graphite bound together with around 10% of a suitable polymer.

The separator/electrolyte **15**, interposed between the positive and negative electrodes is typically around 100 microns thick and is prepared from a polymer having basic or tertiary nitrogen groups in its structure and an electrolyte salt both of which are dissolved in a common solvent. Suitable polymers include poly(vinyl pyridine), poly(vinylpyrrolidone) and poly(acrylonitrile). The electrolyte salt may be one or more chosen from LiBF_4 , LiPF_6 , LiClO_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{Li}(\text{CF}_3\text{SO}_3)$, LiAlCl_4 .

An electrochemical cell having the structure described above may take the form of a coin cell, a wound cylindrical cell or a multifolded prismatic format. The latter is preferred for large cells and supercapacitors. Fig. 2 shows an example of a multiple folded prismatic cell.

Example 1

A cathode was prepared by mixing together lithium cobalt oxide 77 %, Super P carbon 6%, lithium dithionite 10% and PVDF binder 7% all by weight. The binder was first dissolved in N-methyl pyrrolidone as a 4.5 w/v solution. The slurry was coated by doctor blade technique on to aluminium foil 15 microns thick. After solvent removal in an anhydrous atmosphere, the cathode was dried under vacuum at 105°C for 8 hours. The separator/electrolyte was prepared by making up a solution of poly(4-vinylpyridine) and lithium tetrafluoroborate in a mixture of gamma butyrolactone and N-methyl pyrrolidone. This solution was coated by doctor blade technique on to the previously prepared anode already coated on to copper foil. The solvents were removed by heating to 105°C in a dry inert atmosphere for 1 to 2 hours. The anode/separator/electrolyte and the cathode were then laminated together using steel rollers to make a cell as shown in Fig. 1

Example 2

In this example, the same cathode and anode as that of Example 1 was used with a different separator/electrolyte composition. The latter was prepared using anhydrous poly(vinylpyrrolidone) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ dissolved in a mixture of dimethylformamide and propylene carbonate. The solution was coated on to the anode as described in Example 1, dried under vacuum to remove the solvents and then laminated on to the cathode.

Example 3

In this example, the cathode was a composite of vanadium (IV) oxide V_2O_4 and lithium sulphite Li_2SO_3 in a 1:1 molar ratio. The cathode mix was prepared using 85% of this active material, 5% Super P carbon, 6% thermally restructured poly(acrylonitrile) and 4% PVDF binder. The procedure for preparation and coating of the paste were the same as in Example 1. The separator/electrolyte was prepared using poly(acrylonitrile) thermally restructured at 250°C under vacuum and LiCF_3SO_3 . These materials were dissolved in a mixture of N-methyl pyrrolidone and dimethylformamide. The solution was coated on to the anode as described in Example 1, dried under vacuum to remove the solvents and then laminated on to the cathode.

Example 4

In this example, the cathode was prepared by mixing together lithium manganese (III, IV) oxide, LiMn_2O_4 (80%), lithium sulphite (9%), Super P carbon (6%) and PVDF binder (5%) as a 4.5w/v solution in N-methyl pyrrolidone. The cathode mix was coated on to expanded stainless steel foil. The separator/electrolyte was prepared using poly(4-vinylpyridine) and LiAlCl_4 in dimethylformamide. This solution was coated on to the cathode which had previously had the carrier solvent removed under vacuum. Following a further drying operation, the composite cathode and separator/electrolyte was laminated to a lithium foil anode pressed on to a copper foil current collector.

The cells fabricated as described above were charged at a current density of 0.2 ma/cm^2 , to a maximum voltage of 4.2V. After allowing to stand for at least 7 days, the cells were cycled at a current density of 0.5 ma/cm^2 .

On opening up cells that had undergone multiple cycling, there was no evidence of gaseous sulphur dioxide being present. It was concluded that for the examples tested, the polymer electrolyte layer had an excess of N-basic functionality relative to the amount of sulphur dioxide generated *in situ* by the initial charging process.

Claims

1. An electrochemical cell which comprises the following:-
 1. A positive electrode(cathode) which contains a compound MA_xO_y where M is an alkali or alkaline earth metal such as lithium and A is a non metallic element such as sulphur, nitrogen, carbon or phosphorous and $0.5 \leq x \leq 2.0$; $2.0 \leq y \leq 4.0$, such that on charging, the acid anhydride A_xO_y is generated as a fluid.
and
 2. A solid polymer film acting as separator whose structural units contain basic functional groups, particularly nitrogen atoms in a 5 or 6 membered heterocycle ring or in tertiary aliphatic configuration into which is incorporated an ionisable salt MZ, having a higher decomposition voltage than MA_xO_y , where M is the same alkali metal and Z is an acid radical which may be, but not limited to one or more of the following:-
 BF_4 , PF_6 , ClO_4 , CF_3SO_3 , $N(CF_3SO_2)$, $AlCl_4$.
2. An electrochemical cell as claimed in 1, wherein the alkali metal M, is lithium and the element A is sulphur.
3. An electrochemical cell as claimed in 1, wherein the compound MA_xO_y , is lithium dithionite or lithium sulphite.
4. An electrochemical cell of claim 1.2, wherein said solid polymer is poly(4-vinylpyridine), less than 5% cross linked.
5. An electrochemical cell of claim 1.2, wherein said solid polymer is poly(vinylpyrrolidone).
6. An electrochemical cell of claim 1.2, wherein said solid polymer is thermally restructured poly(acrylonitrile) $\{CH=CH-CN\}_n$.
7. An electrochemical cell as described in claims 1 to 6 above may function as a primary or rechargeable battery or as a supercapacitor.

ABSTRACT

The present invention relates to an electrochemical cell having a solid polymer separator/electrolyte whose ion conductivity is markedly increased by in situ generation of a fluid acidic anhydride.

The cell according to this invention comprises a solid polymer electrolyte, an anode of an alkali or alkaline earth metal such as lithium and a cathode containing the lithium or other alkali or alkaline earth metal salt of the acid anhydride to be electrochemically generated in addition to the main active material. The salt which is central to this invention has the formula MA_xO_y where M is an alkali or alkaline earth metal in particular lithium and A is a non metallic element such as sulphur, nitrogen, carbon or phosphorous $0.5 \leq x \leq 2.0$ and $2 \leq y \leq 4$. The cell according to this invention has much improved rate capability and low temperature performance but no liquid constituents are required for assembly of the cell.

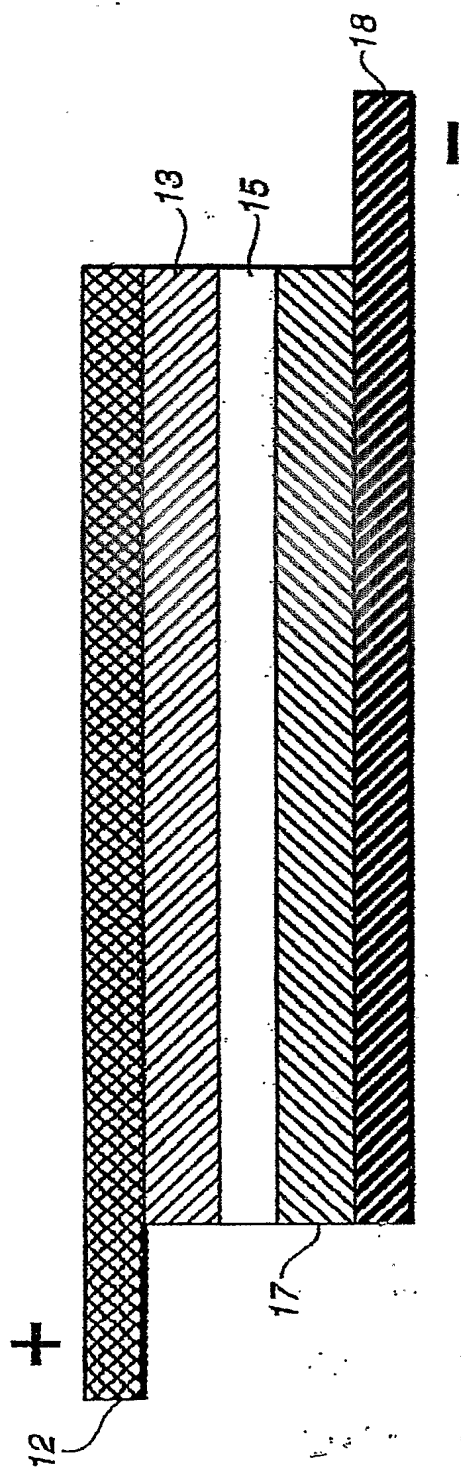


FIG. 1

FIG. 2

